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ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: POLYETHYLENE NETS

(57) Abstract: A net for packaging comprising high density polyethylene, which contains from 0.5 to 10 % by weight of poly-  
isobutene. This imparts additional tackiness to the net, but does not adversely affect the manufacturing process.

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### POLYETHYLENE NETS

The present invention relates to nets made of high density polyethylene (HDPE), such as those typically used for packaging. For transporting containers such as wooden crates or boxes, it is well known to wrap the containers in a web of plastic such as high density polyethylene (HDPE), which may be perforated or in the form of a net. In the present specification, the term "net" means any sheet containing regular apertures or perforations, whether or not it has been woven.

In order to prevent slippage of the containers within the package wrapped by the plastic net, it is desirable that the net has some degree of adhesion to the container surfaces with which it is in contact. It is known to incorporate certain additives into the plastic in order to provide the plastic with a degree of "tackiness". However one disadvantage of such additives is that the tackiness they impart makes processing of the plastic during the manufacture of the nets more difficult.

It is well known to incorporate polyisobutene (PiB) into HDPE, for example as an elastomeric plasticiser, or to improve resistance to stress cracking, or even as a pressure-sensitive adhesive. It is known to incorporate PiB into low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) in order to improve the tackiness of the plastic. However these plastics are not suitable for load-bearing applications such as nets.

We have found that if such nets are made of HDPE, the incorporation of polyisobutene (PiB) into the nets can provide the desired adhesion properties of the final product, without adversely affecting the processing properties of the HDPE during manufacture of the nets.

Accordingly in a first aspect the present invention provides a net for packaging which comprises high density polyethylene and from 0.5 to 10 % by weight of polyisobutene.

It is believed that the advantages of the present invention arise because the added PiB provides the adhesive properties by its presence on the surface of the HDPE : and that it takes about 48 hours after incorporation into the HDPE to migrate to the surface, and up to 5 days for the maximum level of tackiness to develop. Therefore since the HDPE is compounded and converted into a net in a much shorter time than 48 hours, it does not have any additional adhesive properties during that manufacturing process.

In a typical manufacturing process, the HDPE is compounded together with the required amount of PiB, and then extruded or blown to form a film. The film is then cut into tapes which are stretched and then woven or knitted into nets. Alternatively, the compounded HDPE/PiB is extruded into monofilaments or multifilaments, which can be woven into thicker filaments and then stretched and knitted into nets. It is particularly advantageous for the knitting or weaving process that the HDPE does not have any additional adhesive properties during this step.

The amount of PiB in the HDPE is preferably between 2 and 6% by weight. When the HDPE is blown into a film prior to cutting, typical amounts of PiB are between 3 and 6wt%. If the HDPE is extruded into a film, amounts of PiB are typically between 2 and 5wt%.

The HDPE film which is to be formed into tapes is typically made by first blending the PiB with the polyethylene in a mixer or compounding extruder and then pelletising. The pellets are then converted into film in the same way as conventional polyethylene. Alternatively, a "Master Batch" of HDPE (or sometimes LDPE) containing up to 60% by weight PiB is first prepared, and this is compounded with pure HDPE in an amount sufficient to yield the required final concentration of PiB.

The PiB used preferably has a number average molecular weight  $M_n$  of between 1000 and 2500. The viscosity at 100°C preferably ranges between 600 and 3000 cSt. Generally, the higher the molecular weight or viscosity of the PiB, the longer the eventual tackiness takes to appear. The choice of PiB may also depend on the processing temperature; lower processing temperatures generally require lower molecular weight PiBs. For example, blown films typically process at 190-230°C, and

for those, PiBs such as Indopol® H-100 and H-300 available from BP Chemicals may be used. For extruded (slot-cast) film, which can be processed at over 270°C, the higher molecular weight products Indopol® H-1200 H-1500, H-1900 and H-2100 may be used. Indopol® H-300 and H-1200 are most preferred products.

5        Following cooling of the film, it is cut into tapes. The cooling rate of the film can have an effect on the eventual tackiness of the HDPE : generally, the higher the cooling rate the greater the degree of tackiness. Cooling rates above 13°C/second, particularly above 15°C/second, are preferred.

10       Prior to formation into nets, it is preferred that the PiB-containing HDPE is stored at as low a temperature as possible so as to maximise the length of time before the tackiness develops. A preferred storage temperature is below 10°C.

15       The degree of tackiness is typically evaluated by determining two related parameters : peel cling, which measures the ease of peeling apart two surfaces (the separating forces being exerted at 90° to the surfaces), and lap cling, which measures the ease of pulling apart two surfaces where the separating forces are parallel to the surfaces.

      Lap cling is measured by determining the load at "break" when two partially overlapping films of the material of predetermined dimensions are separated by holding one film and placing a weight on the other.

## 20       EXAMPLES

      A "Master Batch" of LDPE containing 60% by weight PiB was prepared, and this was compounded with pure HDPE in amounts sufficient to provide three samples containing different concentrations of PiB as follows:

      Example 1 – 92wt% HDPE + 8wt% Masterbatch giving 4.8wt% PiB

25       Example 2 – 90wt% HDPE + 10wt% Masterbatch giving 6.0wt% PiB

      Example 3 – 88wt% HDPE + 12wt% Masterbatch giving 7.2wt% PiB

      These three samples were extruded as films and then evaluated for peel cling and lap cling.

### Peel cling

30       Peel cling measures the ease of peeling apart two surfaces (the separating forces being exerted at 90° to the surfaces).

      The films were conditioned at 23°C and at 50% relative humidity for a period of

24 hours prior to the evaluation. Then two 25cm x 15cm (machine direction) sheets were cut from the film and placed exactly on top of one another with their inside surfaces facing, except for a 25cm by 4cm sheet of paper interposed between them along one 25cm edge. The two films were totally crease-free.

5        Seven identical 12.5cm by 2.5 cm portions were then cut from a series of such pairs of films, the pair of films in each portion being separated by the inserted paper at one end only. The seven portions were then placed on top of one another with their paper interleaves at the same end, each portion being separated from the next by a sheet of paper. A 2.16 kg weight was placed on the stack of film pairs for 30 minutes.

10        At the end of the 30 minutes, the force required to separate each film pair by pulling on the ends already separated by paper was determined using an Instron machine. Six pairs were tested, and the peel cling determined as average recorded load x 1000/25. The results (an average of the six tests) are shown in the Table below.

#### Lap cling

15        Lap cling measures the ease of pulling apart two surfaces where the separating forces are parallel to the surfaces.

      The films were conditioned at 23°C and at 50% relative humidity for a period of 24 hours prior to the evaluation. Then two 25cm x 15cm (machine direction) sheets were cut from the film, and the first sheet placed, inside surface down, on an aluminium  
20        backing plate on which two parallel lines had been scored 1cm apart, such that the sheet covered both lines and its longer side was parallel to the lines. This longer side was trimmed along the first of the lines to make a clean edge ending at that line. Then, with this first sheet lifted off the backing plate where it covered the two lines, the second sheet was placed, inside surface down, on the backing plate opposite the first, again  
25        such that the sheet covered both lines and its longer side was parallel to the lines. This longer side was also trimmed along the first of the lines to make a clean edge ending at that line.

      Thus with both sheets lying flat on the backing plate, they overlapped by 1cm, the overlap lying exactly between the two scored lines on the backing plate. A 12.5cm x  
30        2.5cm portion was then cut from the overlapping films such that the portion of overlap was in the middle of the cut portion. Six such portions were cut, and were prepared by rolling a 2.16kg weight over them six times.

The force required to separate each film pair by pulling on each end was determined using an Instron machine. Six pairs were tested, and the peel cling determined as the average force. The results are shown in the Table below.

Example	lap cling (OP/511)	peel cling
Example 1 – 4.8wt% PiB	0.82 N/mm	0.58 N/m
Example 2 – 6.0wt% PiB	1.17 N/mm	1.54 N/m
Example 3 – 7.2wt% PiB	1.28 N/mm	3.58 N/m

These results show that increasing the amount of PiB in the HDPE results in an enhancement of both peel cling and lap cling, which equates to increased tackiness when the HDPE is used to make nets.

Claims

1. Net for packaging comprising high density polyethylene, which contains from 0.5 to 10% by weight of polyisobutene.
- 2 - Net according to claim 1, wherein the amount of polyisobutene is from 2 to 6 % by weight.
- 5 3 - Net according to any preceding claim, wherein the polyisobutene has a number average molecular weight  $M_n$  of from 1000 to 2500.
- 4 - Net according to any preceding claim, wherein the polyisobutene has a viscosity at 100°C between 600 and 3000 cSt.
- 5 - Process for manufacturing a net for packaging, comprising compounding together  
10 high density polyethylene and polyisobutene, and converting the resultant polymer into a net.
- 6 - Process according to claim 5, wherein the cooling of the polymer melt after compounding is at a rate of at least 13°C/second.
- 7 - Use of polyisobutene to increase the adhesiveness of nets made of high density  
15 polyethylene.

# INTERNATIONAL SEARCH REPORT

International Application No  
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## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 680 330 A (BERRIER BERNARD ET AL) 14 July 1987 (1987-07-14) abstract column 1, line 5 - line 38 column 1, line 63 -column 2, line 39 column 3, line 53 -column 4, line 27 examples	1-7
Y	US 3 454 455 A (RASMUSSEN OLE-BENDT) 8 July 1969 (1969-07-08) the whole document -/-	1-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 109 512 A (DOW CHEMICAL CO) 30 May 1984 (1984-05-30) abstract page 1, line 1 - line 8 page 2, line 10 - line 17 page 3, line 8 - line 13 page 3, line 14 - line 25 page 4, line 12 - line 27 page 5, line 28 - page 6, line 23 page 8, line 23 - line 25 example 1</p>	1-7
Y	<p>US 4 911 985 A (JENKINS EDWIN A ET AL) 27 March 1990 (1990-03-27) abstract column 1, line 35 - line 50 column 1, line 54 - column 2, line 15 column 6, line 33 - line 48</p>	1-7
Y	<p>EP 0 339 990 A (MITSUI PETROCHEMICAL IND ;SHELL OIL CO (US)) 2 November 1989 (1989-11-02) abstract page 1, line 3 - line 26 page 2, line 46 - page 3, line 33 page 3, line 51 - line 54 page 4, line 32 - line 54 page 5, line 21 - line 35 example 1</p>	1-7
Y	<p>US 5 849 394 A (BUSSEY JR HARRY ET AL) 15 December 1998 (1998-12-15) abstract column 1, line 58 - line 67 column 2, line 17 - line 31 column 2, line 41 - line 43 column 4, line 35 - column 5, line 8</p>	1-7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4680330	A	14-07-1987	FR 2575483 A1 AT 45974 T CA 1272533 A1 DE 3572683 D1 EP 0194383 A1 ES 8801846 A1 ES 8800304 A1 IN 165767 A1 JP 6004729 B JP 61162538 A PT 81763 A ,B SG 76589 G	04-07-1986 15-09-1989 07-08-1990 05-10-1989 17-09-1986 01-05-1988 01-01-1988 06-01-1990 19-01-1994 23-07-1986 02-01-1986 20-04-1990
US 3454455	A	08-07-1969	GB 1103583 A CH 428191 A DE 1266950 B DK 109651 C FI 41455 B FR 1415097 A NL 6413126 A ,B NO 120809 B SE 318098 B	14-02-1968 15-01-1967 25-04-1968 27-05-1968 31-07-1969 22-10-1965 13-05-1965 07-12-1970 01-12-1969
EP 0109512	A	30-05-1984	AU 560972 B2 AU 1875683 A BR 8305429 A EP 0109512 A2 GB 2128199 A ,B JP 59083625 A NZ 205697 A PH 18348 A US 4588650 A	30-04-1987 05-04-1984 15-05-1984 30-05-1984 26-04-1984 15-05-1984 30-04-1987 05-06-1985 13-05-1986
US 4911985	A	27-03-1990	US 5049441 A	17-09-1991
EP 0339990	A	02-11-1989	AT 96828 T AU 3372489 A DE 68910373 D1 DE 68910373 T2 DK 209089 A EP 0339990 A2 JP 1301735 A JP 2660047 B2 NO 891802 A NZ 228914 A	15-11-1993 02-11-1989 09-12-1993 11-05-1994 30-10-1989 02-11-1989 05-12-1989 08-10-1997 30-10-1989 26-10-1990
US 5849394	A	15-12-1998	NONE	